

CLAIMS

1. A ceramic molded body, more specifically a roof tile, tile, clinker brick, or a facade wall of oxide-ceramic base material with a surface which is self-cleaning upon spraying or sprinkling with water, characterised in that the molded body has a porous oxide-ceramic coating, wherein the coating is photocatalytically active and has a specific surface area in a range of between about 25 mg²/g and about 200 m²/g, preferably between about 40 m²/g and about 150 m²/g.

2. A ceramic molded body as set forth in claim 1 characterised in that the oxide-ceramic base material has a capillary structure and the porous, oxide-ceramic coating is applied on the surface and in the pore openings and the free faces of the capillary structure near the surface in the interior of the ceramic molded body.

3. A ceramic molded body as set forth in claim 1 characterised in that the pore openings are of an intergranular and/or intragranular nature.

4. A ceramic molded body as set forth in one of claims 1 through 3 characterised in that the free breathing cross-section of the ceramic molded body is reduced by the applied porous, oxide-ceramic coating by less than 10%, preferably less than 5%, with respect to the free breathing cross-section of an uncoated ceramic molded body.

5. A ceramic molded body as set forth in one of claims 1 through 4 characterised in that the porous, oxide-ceramic coating is applied to a depth of 1 mm, preferably to a depth of 2 mm, measured in a vertical direction from the surface of the ceramic molded body, in the ceramic molded body.

6. A ceramic molded body as set forth in one of the preceding claims characterised in that the coating has a specific surface area in a range of between about 40 m²/g and about 100 m²/g.

7. A ceramic molded body as set forth in one of the preceding claims characterised in that the mean layer thickness of the coating is in a range of between about 50 nm and about 50 µm, preferably about 100 nm and about 1 µm.

8. A ceramic molded body as set forth in one of the preceding claims characterised in that arranged between the oxide-ceramic base material and the photocatalytically active, porous, oxide-ceramic coating is at least one layer with raised portions, the oxide-ceramic base material has raised portions, and/or the photocatalytically active, porous, oxide-ceramic coating is in the form of a layer with raised portions.

9. A ceramic molded body as set forth in claim 8 characterised in that the raised portions are formed by particulate material fixed to the oxide-ceramic base material.

10. A ceramic molded body as set forth in claim 9 characterised in that the particulate material is temperature-resistant ground material preferably selected from the group which consists of ground rock, fire clay, clay, minerals, ceramic powder such as SiC, glass, glass chamotte and mixtures thereof.

11. A ceramic molded body as set forth in claim 9 or claim 10 characterised in that the size of the particles and/or the raised portions is or are in a range of up to 1500 nm, preferably of between about 5 nm and about 700 nm, further preferably between about 5 nm and about 25 to 50 nm.

12. A ceramic molded body as set forth in one of the preceding claims characterised in that the photocatalytically active, porous, oxide-ceramic coating includes photocatalytically active, oxide-ceramic materials selected from the group which consists of TiO_2 , Al_2O_3 , SiO_2 , Ce_2O_3 and mixtures thereof.

13. A ceramic molded body as set forth in one of the preceding claims characterised in that the oxide-ceramic base material of the molded body includes photocatalytically active, oxide-ceramic materials selected from the group which consists of TiO_2 , Al_2O_3 , SiO_2 , Ce_2O_3 and mixtures thereof.

14. A ceramic molded body as set forth in one of claims 12 and 13 characterised in that the photocatalytically active, oxide-ceramic material has an average particle size in the range of between about 5 nm and about 100 nm, preferably between about 10 nm and about 50 nm.

15. A ceramic molded body as set forth in one of claims 12 through 14 characterised in that the TiO_2 contained in the photocatalytically active, porous, oxide-ceramic coating and/or in the oxide-ceramic base material is present at least in part and preferably in respect of at least 40% by weight with respect to the total amount of TiO_2 , in the anatase structure.

16. A ceramic molded body as set forth in claim 15 characterised in that the TiO_2 contained in the photocatalytically active, porous, oxide-ceramic coating and/or in the oxide-ceramic base material is present in respect of at least 70% by weight with respect to the total amount of TiO_2 , in the anatase structure.

17. A ceramic molded body as set forth in one of claims 14 through 16 characterised in that the TiO_2 is present in a mixture comprising between about 70 and 100% by weight of anatase and between about 30 and 0% by weight of rutile.

18. A ceramic molded body as set forth in one of claims 14 through 16 characterised in that the TiO_2 is present in respect of about 100% by weight in the anatase structure.

19. A ceramic molded body as set forth in one of claims 1 through 18 characterised in that the contact angle of a 10 μl drop of water on the porous, oxide-ceramic coating without hydrophobic post-coating after 15 hours of irradiation with 1 mW/cm^2 UV-A black light is less than 6° to 7° , preferably less than 5° , further preferably less than 4° .

20. A ceramic molded body as set forth in one of claims 1 through 19 characterised in that the contact angle of a 10 μl drop of water on the porous, oxide-ceramic coating without hydrophobic post-coating after 15 hours of irradiation with 1 mW/cm^2 UV-A black light and 30 days in darkness is less than 20° , preferably less than 18° , further preferably less than 14° .

21. A ceramic molded body as set forth in one of claims 1 through 20 characterised in that the contact angle of a 10 μl drop of water on the porous, oxide-ceramic coating without hydrophobic post-coating after 15 hours of irradiation with 1 mW/cm^2 UV-A black light and 30 days in darkness and renewed irradiation with preferably 1 mW/cm^2 UV-A black light for 3 hours is less than 8° , preferably less than 7° .

22. A ceramic molded body as set forth in one of the preceding claims characterised in that the coating has a superhydrophobic surface.

23. A coarse-ceramic ceramic molded body as set forth in claim 22 characterised in that the superhydrophobic surface is provided using one or more compounds having straight-chain or branched-chain aromatic and/or aliphatic hydrocarbon residues with functional groups, wherein the

functional groups are selected from amine, thiol, a carboxyl group, alcohol, disulfide, aldehyde, sulfonate, ester, ether or mixtures thereof.

24. A ceramic molded body as set forth in claim 23 characterised in that the superhydrophobic surface is produced using compounds selected from the group which consists of silicone oil, amine oils, silicone resin, for example alkylpolysiloxanes, alkoxysiloxanes, alkali metal siliconates, alkaline earth siliconates, silane-siloxane mixtures, amino acids and mixtures thereof.

25. A ceramic molded body as set forth in claim 22 characterised in that the superhydrophobic surface of the coating is produced using Ormoceres, polysiloxane, alkylsilane and/or fluorosilane, preferably in combination with SiO_2 .

26. A ceramic molded body as set forth in claim 22 characterised in that the superhydrophobic surface is applied using a solution of alkali metal siliconates in water, wherein alkali metal is selected from the group which consists of lithium, sodium, potassium and mixtures thereof.

27. A ceramic molded body as set forth in one of claims 22 through 26 characterised in that the superhydrophobic surface has a contact or edge angle of at least 140° for water.

28. A ceramic molded body as set forth in one of claims 22 through 27 characterised in that the superhydrophobic surface has a contact or edge angle of at least 150° for water, preferably at least 160° , still further preferably at least 170° .

29. A ceramic molded body as set forth in claim 26 characterised in that the solution of alkali metal siliconates in water has a dilution ratio of between 1:100 and 1:600 (by weight/by weight), preferably a dilution ratio of between 1:250 and 1:350 (by weight/by weight).

30. A ceramic molded body as set forth in one of claims 22 through 29 characterised in that the superhydrophobic surface of the coating has raised portions.

31. A ceramic molded body as set forth in claim 30 characterised in that the raised portions of the superhydrophobic surface are produced using particulate material.

32. A ceramic molded body as set forth in claim 22 characterised in that the superhydrophobic surface is applied using a mixture of particles, for example SiO_2 , and hydrophobising agent, for example fluorosilane.

33. A ceramic molded body as set forth in one of claims 1 through 32 characterised in that the photoefficiency calculated from photocatalytically induced methylene blue breakdown in the case of the porous, oxide-ceramic coating is at least 0.015%, preferably at least 0.02%, further preferably at least 0.03%, still further preferably at least 0.04%.

34. A process for the production of a coarse-ceramic molded body, preferably of oxide-ceramic base material with a capillary structure and with a surface which is self-cleaning upon spraying or sprinkling with water, wherein the molded body has a photocatalytically active, porous, oxide-ceramic coating with a specific surface area in a range of between about 25 m^2/g and about 200 m^2/g , preferably about 40 m^2/g and about 150 m^2/g , and the porous oxide-ceramic coating is disposed on the surface and in the pore openings and the free faces of the capillary structure near the surface in the interior of the coarse-ceramic molded body,

wherein the process includes the following steps:

(a) mixing photocatalytically active, oxide-ceramic powder, inorganic stabilisation agent and a liquid phase to afford a suspension,

(b) applying the suspension produced in step (a) to the oxide-ceramic base material to produce a layer, and

(c) hardening the layer afforded in step (b) to produce a photocatalytically active, porous, oxide-ceramic coating.

35. A process as set forth in claim 34 characterised in that at least one layer with raised portions is applied to the oxide-ceramic base material in a preceding step and the suspension produced in step (a) is applied to the oxide-ceramic base material provided with a layer with raised portions and subsequently hardened in step (c).

36. A process as set forth in one of claims 34 and 35 characterised in that particulate material is additionally added in step (a).

37. A process as set forth in claim 35 or claim 36 characterised in that raised portions are formed by fixing particulate material on the oxide-ceramic base material.

38. A process as set forth in claim 36 or claim 37 characterised in that the particulate material is temperature-resistant ground material preferably selected from the group which consists of ground rock, fire clay, clay, minerals, ceramic powder such as SiC, glass, glass chamotte and mixtures thereof.

39. A process as set forth in one of claims 36 through 38 characterised in that the mean particle size of the particulate material is in a range of up to about 1500 nm, preferably between about 5 nm and 700 nm, further preferably between about 5 nm and about 25 to 50 nm.

40. A process as set forth in one of claims 34 through 39 characterised in that the inorganic stabilisation agent used in step (a) stabilises the photocatalytically active, oxide-ceramic powder particles in the suspension so that the photocatalytically active, oxide-ceramic powder particles do not precipitate and/or do not agglomerate.

41. A process as set forth in claim 40 characterised in that SiO_2 , SnO_2 , $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 or mixtures thereof are used as the inorganic stabilisation agent.

42. A process as set forth in one of claims 34 through 41 characterised in that adhesive, preferably polysiloxane, is added to the suspension in step (a).

43. A process as set forth in one of claims 34 through 42 characterised in that water or an aqueous or water-bearing medium is used as the liquid phase in step (a).

44. A process as set forth in one of claims 34 through 43 characterised in that the adhesion between the catalytically active coating and the oxide-ceramic base material is improved by a procedure whereby the photocatalytically active, porous, oxide-ceramic coating produced in step (c) is irradiated with laser light or NIR or UV light.

45. A process as set forth in one of claims 34 through 44 characterised in that the photocatalytically active, oxide-ceramic powder used in step (a) includes materials selected from the group which consists of TiO_2 , Al_2O_3 , SiO_2 , Ce_2O_3 and mixtures thereof.

46. A process as set forth in one of claims 34 through 45 characterised in that contained in the oxide-ceramic base material of the molded body are photocatalytically active, oxide-ceramic materials selected from the group which consists of TiO_2 , Al_2O_3 , SiO_2 , Ce_2O_3 and mixtures thereof.

47. A process as set forth in one of claims 34 through 46 characterised in that the photocatalytically active, oxide-ceramic powder used in step (a) includes particles in the range of between about 5 nm and about 100 nm, preferably between about 10 nm and about 50 nm.

48. A process as set forth in one of claims 45 through 47 characterised in that the TiO_2 contained in the photocatalytically active, oxide-ceramic powder and/or in the oxide-ceramic base material is present at least in part and preferably in respect of at least 40% by weight with respect to the total amount of TiO_2 in the anatase structure.

49. A process as set forth in one of claims 45 through 48 characterised in that the TiO_2 contained in the photocatalytically active, oxide-ceramic powder and/or in the oxide-ceramic base material is present in respect of between at least 70% and 100% by weight with respect to the total amount of TiO_2 in the anatase structure.

50. A process as set forth in one of claims 45 through 49 characterised in that the TiO_2 contained in the photocatalytically active, oxide-ceramic powder and/or in the oxide-ceramic base material is present in a mixture comprising between about 70 and 100% by weight of anatase and between about 30 and 0% by weight of rutile.

51. A process as set forth in one of claims 45 through 50 characterised in that the TiO_2 contained in the photocatalytically active, oxide-ceramic powder and/or in the oxide-ceramic base material is present in respect of about 100% by weight with respect to the total amount of TiO_2 in the anatase structure.

52. A process as set forth in one of claims 34 through 51 characterised in that the layer produced in step (b) is hardened in step (c) by drying at a temperature of up to 300°C and/or by calcining at a temperature of more than 300°C to about 1100°C .

53. A process as set forth in claim 52 characterised in that the layer produced in step (b) is at least partially pre-dried prior to the calcining operation in step (c) by evaporation of the liquid phase.

54. A process as set forth in one of claims 34 through 53 characterised in that the coating hardened in step (c) is hydrophobised or superhydrophobised to provide a hydrophobic surface.

55. A process as set forth in one of claims 34 through 54 characterised in that a hydrophobising agent is additionally added in step (a) and the coating produced in step (b) is hardened in step (c) by drying at a temperature of up to 300°C.

56. A process as set forth in claim 54 characterised in that an inorganic-organic hybrid molecule, preferably a polysiloxane solution or an alkali metal or alkaline earth silicate solution is used for hydrophobisation.

57. A process as set forth in claim 54 characterised in that the superhydrophobic surface is provided using one or more compounds having straight-chain or branched-chain aromatic and/or aliphatic hydrocarbon residues with functional groups, wherein the functional groups are selected from amine, thiol, a carboxyl group, alcohol, disulfide, aldehyde, sulfonate, ester, ether or mixtures thereof.

58. A process as set forth in claim 57 characterised in that the superhydrophobic surface is produced using compounds selected from the group which consists of silicone oil, amine oils, silicone resin, for example alkylpolysiloxanes, alkoxysiloxanes, alkali metal silicates, alkaline earth silicates, silane-siloxane mixtures, amino acids and mixtures thereof.

59. A process as set forth in claim 54 characterised in that the superhydrophobic surface of the coating is produced using Ormoceres, polysiloxane, alkylsilane and/or fluorosilane, preferably in a mixture with SiO₂.

60. A process as set forth in one of claims 54 through 59 characterised in that particulate material is added to produce a superhydrophobic surface with raised portions in the hydrophobisation operation.

61. A process as set forth in one of claims 34 through 60 characterised in that the coarse-ceramic molded body is a roof tile, tile, clinker brick or a facade wall.

Abstract

The invention concerns a ceramic molded body, more specifically a roof tile, tile, clinker brick, or a facade wall of oxide-ceramic base material with a surface which is self-cleaning upon spraying or sprinkling with water, wherein the molded body has a porous oxide-ceramic coating, wherein the coating is photocatalytically active and has a specific surface area in a range of between about 25 m²/g and about 200 m²/g, preferably between about 40 m²/g and about 150 m²/g. The invention further concerns a process for producing such a coarse-ceramic molded body.